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SACRAMENTO PLANT

INVESTIGATIONS OF THE MECHANISMS
OF DECOMPOSITION, COMBUSTION, AND DETONATION
OF SOLIDS

REPORT NO. 0372-01-19Q

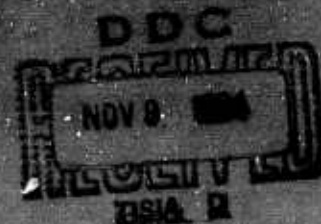
OCTOBER 1964

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AEROJET-GENERAL CORPORATION

SACRAMENTO, CALIFORNIA



INVESTIGATIONS OF THE MECHANISMS
OF DECOMPOSITION, COMBUSTION, AND DETONATION
OF SOLIDS

A Report To
Director of Aeronautical Sciences
Air Force Office of Aerospace Research

CONTRACT AF 49(638)-851
OSR Project No. 9750, Task 37501
ARPA Order No. 24-60, Project No. 4759


Report No. 0372-01-19Q

October 1964

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This is the nineteenth quarterly Technical Operating Report submitted in partial fulfillment of the contract. It covers the period 1 July through 30 September 1964.

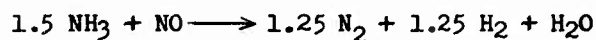
AEROJET-GENERAL CORPORATION

for 
L. J. Rosen, Acting Manager
Propellant Research Division
Solid Rocket Operations

ABSTRACT

Apparent flame strength (AFS) measurements have been made on the ammonia-nitric oxide and ammonia-nitrous oxide flame reactions in the opposed-jet reactor at pressures ranging from 100 to 745 torr. The pressure dependencies of the apparent flame strengths of these systems gave overall reaction orders of 1.56 and 2.0 for $\text{NH}_3\text{-NO}$ and $\text{NH}_3\text{-N}_2\text{O}$ counterflow diffusion flames, respectively.

The overall stoichiometry of the $\text{NH}_3\text{-NO}$ flame near extinguishment can be represented by the following equation.



The volumetric reaction rate ($\dot{M}_{\text{fu}}^{\text{'''}}$, max) for this flame reaction was computed using Spalding's analysis of the opposed-jet flame. At 1 atmosphere, an apparent flame strength of $0.65 \text{ gm/cm}^2\text{-sec}$ corresponded to volumetric reaction rate of $2.93 \text{ gm/cm}^3\text{-sec}$ release rate of $7.22 \times 10^3 \text{ cal/cm}^3\text{-sec}$.

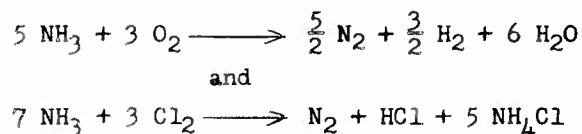
I. INTRODUCTION

The objective of the research being conducted under this contract, funded by the Advanced Research Projects Agency, is to obtain a better understanding of the mechanisms of combustion, decomposition, and detonation of solids. Current investigations are concerned with the gas-phase reactions associated with the combustion of composite solid propellants and their relationships to the energy transport processes near solid-propellant surfaces.

II. TECHNICAL STATUS

A. SUMMARY OF PREVIOUS WORK

The flame reaction between NH_3 and $\text{O}_2\text{-Cl}_2$ mixtures was studied by means of the opposed-jet technique. This flame system is being investigated because it is believed that the kinetics of the gas-phase reactions above burning ammonium perchlorate (AP) are dependent primarily upon the competition between the two irreversible reactions:



It was shown that $\text{NH}_3\text{-O}_2\text{-Cl}_2$ flames exist for large mass fractions of chlorine (up to m.f. = 0.6), however, apparent flame strength (AFS) measurements were not feasible at Cl_2 m.f. > 0.56 due to flame out before axial extinguishment could occur. The apparent flame strengths of these flames were inversely proportional to the mass fraction of chlorine and directly proportional to the mass fraction of chlorine and directly proportional to mass fractions of oxygen and ammonia in the initial reaction mixtures. However, at mass fractions > 0.4 , < 0.2 and < 0.4 for Cl_2 , O_2 and NH_3 , respectively, the AFS varied only slightly with relatively large changes in concentrations of reactants.

B. CURRENT AND PLANNED WORK

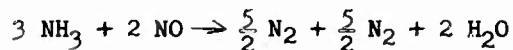
The gas-phase redox reactions which are believed to occur above the surface of decomposing or subliming solid composite propellants containing ammonium perchlorate (AP) are being investigated. The proposed mechanism (Reference 1) for the deflagration of AP stipulates that the overall kinetics of the $\text{NH}_3 - \text{HClO}_4$ is governed primarily by the competition between O_2 and Cl_2 for the NH_3 . Other irreversible reactions which are also believed to be involved are the oxidation of NH_3 by NO and N_2O . These reactions are currently being investigated by means of the opposed-jet technique, which has been described previously (References 2 and 3).

1. Combustion of Ammonia with Nitric Oxide

The $\text{NH}_3\text{-NO}$ counterflow diffusion flame was found to be quite stable and easily ignited; however, at pressures below 150 torr, the flame exhibited some instability and AFS measurements were not feasible for a nozzle diameter of 0.77 cm. Figure 1 tabulates the conditions and apparent flame strength data for the $\text{NH}_3\text{-NO}$ system. A log-log plot (Figure 2) of the AFS versus pressure data is linear and indicates that the overall reaction order is 1.56 at pressures ranging from 150 to 745 torr. This value is in good agreement with that found by Wise and Frech (Reference 4) who investigated this reaction by another technique and reported an overall reaction order of 1.5; first order with respect to NH_3 and one-half order with respect to NO . Volders and van Tiggelen (Reference 5) on the other hand report the reaction to be 1.3 order with respect to NO and 0.5 order with respect to NH_3 (1.8 overall). Although there is mild disagreement concerning the overall order of this reaction, there appears to be considerable disparities among the results of the various studies regarding

the reaction orders with respect to NH_3 and NO .

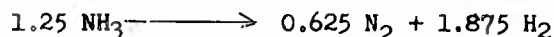
Initial studies have been made to determine the overall stoichiometry of the NH_3 - NO flame reaction. Figure 3 lists the results of mass spectrographic analyses of representative samples of the reaction products sampled downstream from the flames. The sampling techniques are such that the values for H_2O concentrations are inaccurate; consequently, the hydrogen-nitrogen ratio has been utilized in determining the overall stoichiometry. This procedure is valid since all of the oxygen in the reaction products appears in the water. The H_2/N_2 ratio (Figure 3) does not exhibit a pressure dependency indicating constancy of flame temperature over this pressure range (150 to 745 torr). However, the observed ratio of ≈ 0.7 is not in complete agreement with the value (1.0) predicted on the basis of the stoichiometry determined from the NH_3/NO ratio (≈ 1.5) at flame extinguishment. An overall stoichiometry based on the H_2/N_2 of 0.7 predicts an NH_3/NO ratio of 1.0 with unreacted oxygen appearing in the products in order to give a correct mass balance. In as much as no oxygen was detected in the products and an NH_3/NO ratio of 1.0 involves too great an error in the NH_3/NO measurement, it is believed that the stoichiometry based upon the NH_3/NO ratio at extinguishment is the more accurate one and that the measured H_2/N_2 ratio is in error. The overall stoichiometry of the NH_3 - NO counterflow diffusion flame (at extinguishment) can be represented by the following equation.



Actually, in such an NH_3 rich flame, the stoichiometry of combustion can be represented by a combination of two reactions.

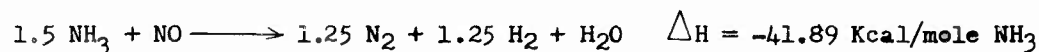


and



These equations indicate that the stoichiometric proportion of NH_3 was oxidized and the excess NH_3 (1.25 moles) decomposed into N_2 and H_2 . A significant result of the AFS measurements is that the NH_3/NO ratio (at extinguishment) in counterflow diffusion flames does not correspond to the ratio (0.828) for the mixture giving the maximum laminar flame speed (S_u).

The volumetric rate of reaction of ammonia for the reaction



has been calculated on the basis of Spalding's analysis of opposed-jet flames (Reference 6) by the expression:

$$\dot{M}_{\text{fu}, \text{max}}''' = \frac{\rho \rho_{\infty} U_{\text{ext}}}{\rho_{\infty} D} \frac{M_{\text{fu}, \infty}}{2 \bar{\Psi}_{\text{st}}} \frac{\Omega_{\text{st}}^2}{f_{\text{st}}}$$

where

$\dot{M}_{\text{fu}, \text{max}}''' =$ the maximum volumetric rate of consumption of the fuel ($\text{g}/\text{cm}^3\text{-sec}$)

$\rho =$ density of fuel

$\rho/\rho_{\infty} =$ fractional density of the fuel in the local mixture

$\rho_{\infty} U_{\text{ext}} =$ apparent flame strength at 1 atmosphere (laminar flow)

$D =$ jet diameter

$M_{\text{fu}, \infty} =$ mass fraction of fuel in the fuel stream

$f_{\text{st}} =$ stoichiometric mass fraction of fuel in the local mixture

$\Omega =$ a dimensionless function of f indicative of the burning rate in the flame

$\bar{\Psi} =$ dimensionless reaction-rate function.

Substitution of the appropriate values in the above expression yields a value for $\dot{M}_{fu, \max}''' \approx 2.93 \text{ g/cm}^3\text{-sec}$ for the $\text{NH}_3\text{-NO}$ reaction at 1 atmosphere. The heat release ratio (\dot{q}_{\max}''') corresponding to this volumetric rate is $7.22 \times 10^3 \text{ cal/cm}^3\text{-sec}$.

2. Combustion of Ammonia with Nitrous Oxide

On the basis of the proposed mechanism of ammonium perchlorate deflagration, opposed-jet experiments have been initiated to investigate the reaction of NH_3 with N_2O . This flame is also quite stable, down to pressures near 100 torr (for nozzle diameter of 0.77 cm). Figures 4 and 5 summarize the results obtained to date for this flame reaction.

A comparison of these data with those obtained for the $\text{NH}_3\text{-NO}$ reaction shows that the apparent flame strength (at 1 atmosphere) of the $\text{NH}_3\text{-N}_2\text{O}$ flame is approximately 3.5 times that for the $\text{NH}_3\text{-NO}$ flame. Considering their respective adiabatic flame temperatures (2580 and 2710°K), this is somewhat surprising. However, before adequate comparisons can be made regarding the contrasts between these two oxidants, additional data will be required, particularly the overall stoichiometry of the $\text{NH}_3\text{-N}_2\text{O}$ flame reaction. These results will be discussed at a later date.

3. Publications

Three papers describing recent and theoretical and experimental achievements have been completed and are being processed for publication. The titles and disposition of these papers are as follows:

"Kinetics of the Decomposition of Anhydrous Perchloric Acid", by D. J. Sibbett and I. Geller. (Submitted to the Journal of Physical Chemistry, September 1964).

"A Model for Low Pressure Extinction of Solid Rocket Motors", by R. F. Chaiken (Submitted to the American Institute of Aeronautics and Astronautics, October 1964).

"Surface Rate Processes and Sensitivity of Solid High Explosives", by R. F. Chaiken and F. J. Cheselske (To be submitted to the Journal of Chemical Physics in November 1964).

A fourth paper, entitled:

"The Reactions of Ammonia with Oxygen and Chlorine in the Opposed-Jet Diffusion Flame", by F. J. Cheselske, D. J. Sibbett and R. F. Chaiken, is in preparation.

4. Future Work

Additional flame studies of the reaction of ammonia with the oxides of nitrogen (N_2O and NO_2) will be made with the object of determining the overall stoichiometries of these reactions in the region of extinguishment.

Theoretical studies of the theory of flame strength in opposed-jet diffusion flames will be continued.

III. PROJECT PERSONNEL

During the period covered by this report, the following personnel contributed the indicated portions of their time to the program

	<u>Time, %</u>
F. J. Cheselske, Principal Investigator	100
R. F. Chaiken, Technical Consultant	30
R. S. Dodds, Senior Laboratory Technician	30

REFERENCES

1. Aerojet-General Corporation, "Investigation of the Mechanisms of Decomposition, Combustion, and Detonation of Solids," Reports 0372-01-12Q - 31 December 1962 and 0372-01-13Q - 31 March 1963; Contract AF 49(638)-851.
2. A. E. Potter and J. N. Butler, ARS Journ., 29, 54-60 (1959).
3. E. Anagnostou and A. E. Potter, "Flame Strength of Propane - Oxygen Flames at Low Pressures in Turbulent Flow," Ninth Symposium (International) on Combustion, Academic Press, New York 1963, pp. 1-6.
4. H. Wise and M. W. Frech, J. Chem. Phys., 22, 1463 (1954).
5. A. Volders and A. van Tiggelen, Bull. Soc. Chim. Belg., 63, 542 (1954).
6. D. B. Spalding, ARS Journ., 31, 763 (1961).

(Nozzle diameter = 0.77 cm)

		Identification Number																		
		20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38
Reactor	Pressure, Torr	300	350	400	450	500	550	600	650	250	200	150	175	200	225	250	275	300	325	71.5
NH ₃ Flow Rate,*	moles/min	0.106	0.135	0.168	0.186	0.226	0.259	0.315	0.355	0.0714	0.059	0.046	0.040	0.052	0.064	0.076	0.096	0.110	0.125	0.166
NO Flow Rate,*	moles/min	0.068	0.084	0.108	0.132	0.145	0.165	0.192	0.218	0.045	0.036	0.028	0.031	0.037	0.044	0.051	0.061	0.068	0.077	0.290
Mole ratio,*	NH ₃ /NO	1.56	1.61	1.56	1.42	1.55	1.57	1.64	1.62	1.64	1.64	1.64	1.29	1.10	1.15	1.19	1.57	1.62	1.62	1.60
AF ₂ **		0.139	0.173	0.221	0.258	0.296	0.338	0.408	0.462	0.694	0.075	0.058	0.059	0.072	0.086	0.101	0.124	0.142	0.166	0.650
AF ₂ ***		0.085	0.106	0.135	0.158	0.181	0.206	0.249	0.282	0.057	0.046	0.036	0.036	0.044	0.052	0.062	0.076	0.087	0.101	0.367

* Value at extinguishment. Average value of NH_3/NO for all experiments in approximately 1.5.

*** Apparent flame strength (laminar flow).
*** Apparent flame strength (turbulent flow).

AMMONIA-NITRIC OXIDE FLAMES
Nozzle Diameter = 0.77 Cm
Laminar Flow

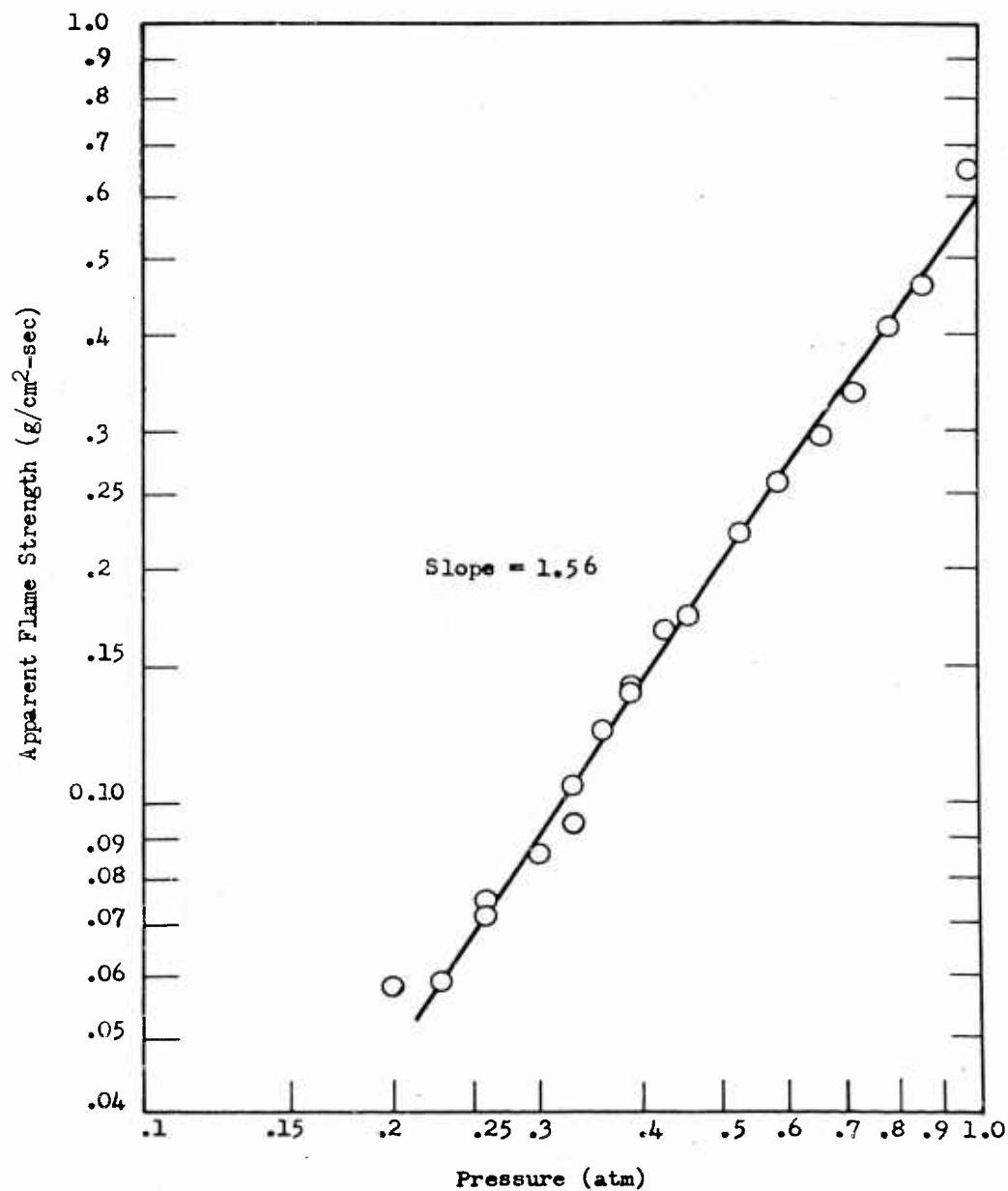


Figure 2

REACTION PRODUCTS FROM AMMONIA - NITRIC OXIDE FLAMES
(MASS SPECTROGRAPHIC ANALYSES)

Identification Number	Pressure, Torr	<u>N₂</u>	<u>H₂</u>	<u>H₂O*</u>	<u>NO**</u>	<u>NH₃</u>	<u>H₂/N₂</u>
20	300	56.0	41.0	2.97	-	-	0.73
23	450	57.9	40.7	1.40	-	<0.3	0.70
27	650	53.9	38.4	-	7.7	-	0.71

* These values are inaccurate due to sampling technique.

** Unreacted.

Figure 3

REACTION CONDITIONS FOR OPPOSED - JET FLAMES
BETWEEN ACETONA AND NITROUS OXIDE

(Nozzle diameter = 0.77 cm)

	Identification Number																		
	31	32	33	34	35	36	37	38	39	40	40-1	45	46	47	48	49	50		
Reactor Pressure, torr	100	150	200	350	400	450	500	550	600	650	745	175	225	275	250	300	325		
NH ₃ Flow Rate, moles/min	0.048	0.073	0.102	0.344	0.506	0.603	0.724	0.818	0.932	1.050	1.444	0.093	0.124	0.209	0.164	0.262	0.324		
H ₂ O Flow Rate, moles/min	0.026	0.040	0.057	0.204	0.268	0.331	0.417	0.489	0.539	0.764	0.907	0.048	0.075	0.126	0.093	0.144	0.174		
Mole Ratio, * NH ₃ /H ₂ O	1.85	1.83	1.79	1.69	1.89	1.82	1.74	1.67	1.73	1.37	1.59	1.94	1.65	1.66	1.76	1.82	1.86		
AFS**	0.044	0.108	0.153	0.534	0.735	0.895	1.106	1.278	1.428	1.861	2.326	0.134	0.195	0.328	0.249	0.390	0.476		
AFS***	0.027	0.066	0.093	0.326	0.449	0.547	0.676	0.780	0.872	1.137	1.421	0.082	0.119	0.200	0.152	0.238	0.291		

* Value at extinguishment. Average value of NH₂/H₂O for all experiments is 1.74.
** Apparent flame strength (laminar flow).
*** Apparent flame strength (turbulent flow).

Figure 2

AMMONIA-NITROUS OXIDE FLAMES
Nozzle Diameter = 0.77 Cm
Laminar Flow

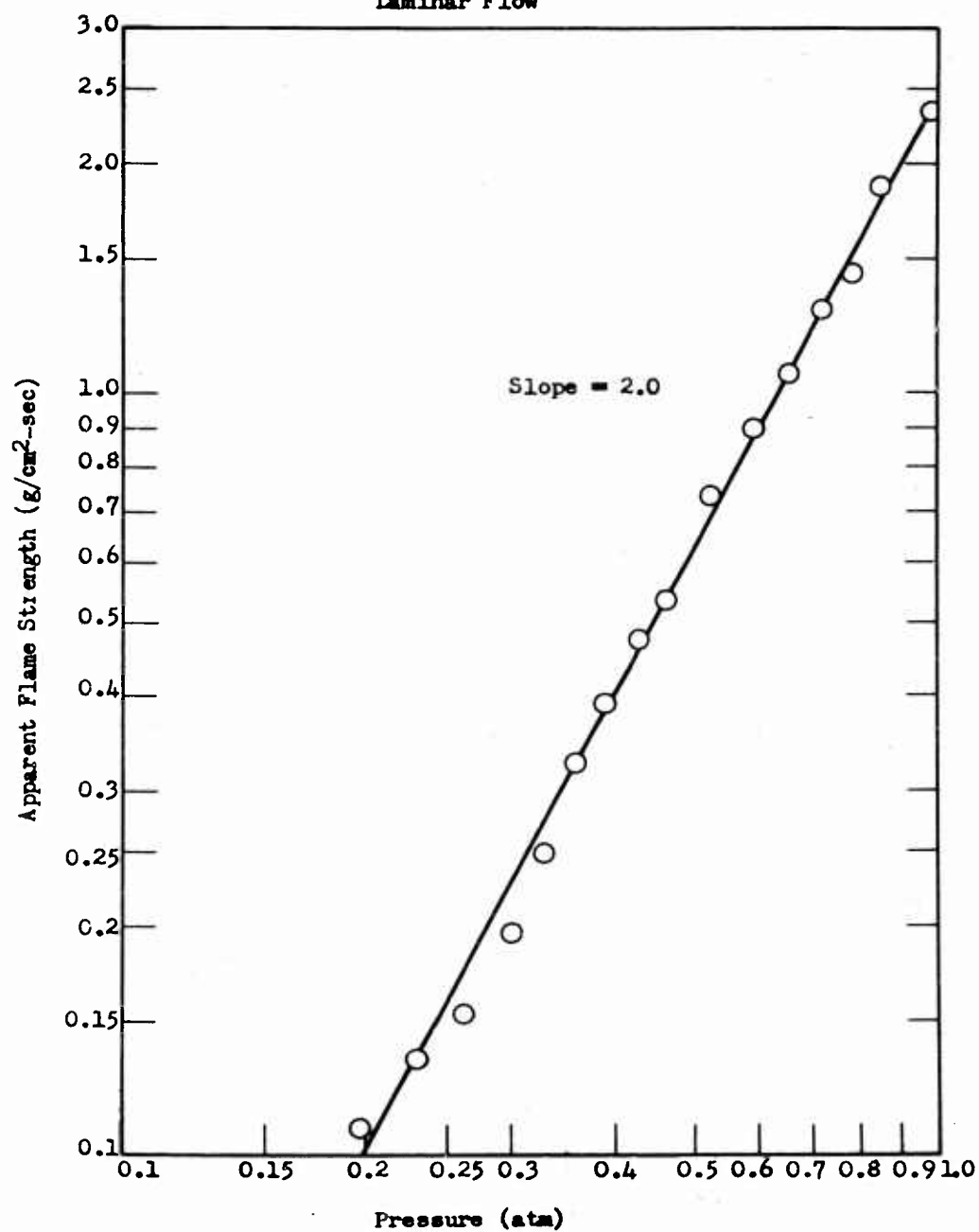


Figure 5.